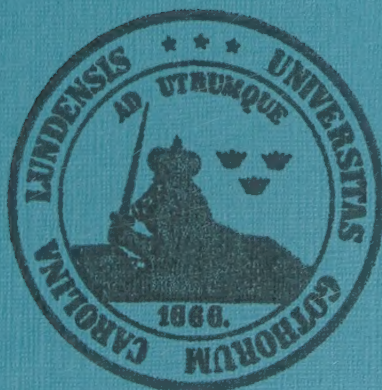


Studies of spark spectra
of sulphur

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Abstract The spectrum of five times ionized sulphur has been studied in the wavelength region 100 - 8000 Å by means of a sliding spark in vacuum. About 90 lines are now attributed to the system, some 70 % which are classified for the first time. The ionization limit derived from a polarization formula based on f, g and h terms is in accordance with Ritz formulae applied to the ns, np and nd series. The spectrum of four times ionized sulphur has been studied in the wavelength region 130 - 7800 Å by means of a sliding vacuum spark. About 385 lines have been identified, 300 of which are new, and many new terms have been established. Some 30 intersystem lines have been found, fixing the triplet system relative to the singlet system. The ionization limit has been derived by means of a polarization formula applied to the 3snh and 3sni series.			
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STUDIES OF SPARK SPECTRA OF SULPHUR

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Studies of Spark Spectra of Sulphur

This thesis consists of two papers:

1. The Spectrum and Term System of S VI

Physica Scripta 20, 145 (1979)

2. The Spectrum and Term System of S V

Physica Scripta (in press)

1. Introduction

The spectra of four and five times ionized sulphur were first studied by I.S. Bowen and R.A. Millikan in 1925 [1,2]. The analyses were extended by Bowen in 1932 and by H.A. Robinson in 1937 [3,4]. Several beam-foil groups have been working on sulphur in recent years and contributed to the knowledge of these spectra [5]. In spite of this, substantial parts of these spectra were either incompletely known or unknown when this investigation was started.

This work on the spectra of S V and S VI is part of a comprehensive investigation of the atomic spectra of elements in the first part of the periodic table which has been in progress at our department for many years under the direction of Professor B. Edlén. The preceding investigations in the Na I - Al I isoelectronic sequences were carried out by C.E. Magnusson and P.O. Zetterberg [6,7,9] who studied multiply ionized phosphorus.

This thesis consists of two papers:

1. The Spectrum and Term System of $2V$
Physics Scripta 50, 145 (1973)

2. The Spectrum and Term System of $2V$
Physics Scripta (in press)

1. Introduction

The spectra of two and five line doublets and triplets were first studied by L.S. Brown and R.A. Millikan in 1925 [1,2]. The analyses were extended by Brown in 1933 and by R.A. Robinson in 1947 [3,4]. Several other groups have been working on similar problems in recent years and contributed to the knowledge of these spectra [5]. In spite of this, substantial parts of these spectra were either incompletely known or unknown when this investigation was started.

This work on the spectra of $2V$ and $2V'$ is part of a comprehensive investigation of the atomic spectra of elements in the first part of the periodic table which has been in progress at our department for many years under the direction of Professor B. Edlén. The preceding investigations in the $2V$ - $2V'$ isoelectronic sequence were carried out by G.E. Kraghsvik and F.O. Zetterberg [6,7] who studied mainly the first phenomena.

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Since all spectra in the Mg I- and Na I-sequences up to P IV and P V were well known, reliable isoelectronic extrapolations to the corresponding sulphur spectra could be made in many cases. As to the experimental work certain experience can also be extrapolated from phosphorus to sulphur spectra. Therefore, it was decided that Zetterberg and Magnusson should take care of the practical guidance of my work. On the basis of their previous knowledge, we could plan the series of exposures that had to be taken under different conditions and with different spectrographs as well as the optimization of the light source and the exposure conditions. The experimental work as well as the analysis was mainly performed by myself.

2. Experiments

In the VUV-region ($\lambda < 2000 \text{ \AA}$) a 3 m normal incidence spectrograph was used between 250 and 2500 $\text{\AA}$ and a 5 m grazing incidence spectrograph for wavelengths between 130 and 400 $\text{\AA}$. The light source is analogous to that used for phosphorus, i.e. a sliding spark in vacuum with beryllium electrodes. In the present cases sulphur was melted into holes at the top of the electrodes. However, problems arose during long exposures in that the electrodes ran out of sulphur and the electrical contact in the spark gap failed. Sometimes the sulphur suddenly melted away, beryllium being a poor heat conductor. By improving the cooling and making the upper electrode holder elastic the conditions were improved so that strong exposures

could be achieved.

The spectra studied in this thesis include lines in the region 150 to 6800 Å. When I started the work above 2000 Å with our 6.4 m Wadsworth mounted Jarrell-Ash spectrograph, I tried a light-source enclosed in an envelope made of glass. This light source had earlier been successfully used together with this spectrograph but turned out to be unsuitable for sulphur. In spite of effective cooling the energy deposit in the light source led to too great a strain on the glass walls near the electrode holders. Instead the metal light source used with the vacuum spectrograph (see Fig. 1 in paper 1) was equipped with a long tube and a quartz window so that it could be used with the Jarrell-Ash spectrograph as well. However, drops and vapour of sulphur from the electrodes clogged the quartz window and made it opaque for the light from the spark gap. By connecting a heating wire to the outside surface of the window the sulphur layer could be boiled off from the inside. The presence of atomic sulphur vapour inside the light source is also evident from self reversal. Reversed line profiles are observed for strong sulphur lines.

On each plate a number of spectrograms were recorded, each optimized to give best line profiles and maximum intensity to one ionization stage. For order separation I used a LiF window when working with the normal incidence vacuum spectrograph and Jena glass filters with the Jarrell-Ash spectrograph. Measurements from the second and third orders were used to obtain high accuracy for the wavelengths of strong lines. A total of about 200 plates were

exposed and much time was spent on the measurements of this vast material. This task as well as the work with assembling the measurements into a comprehensive line list was carried out chiefly by Monica Andersson and myself. The list was furnished with experimental ionization stages judged from line intensities and profiles as a function of the inductance in the discharge circuit. This work was carried out by Zetterberg. Mean values, mean errors, standard deviations and wavenumbers were calculated by standard programs, listed and stored in the UNIVAC computer of Lund Data Center.

3. The spectrum and term system of S VI

The analysis was started by the investigation of S VI. The results is given in paper 1. All identifications made by Robinson [4] were confirmed.

Since S VI is a member of the Na I-sequence with only one valence electron outside the closed $n = 2$ shell, Ritz formulae are reliable for the extrapolation of term values. When the first three members of a series were known Ritz formulae were used to predict the positions of higher terms. For this purpose I modernized a program of a table calculator to fit the UNIVAC-computer. When more term values were known than required to determine the parameters of the formula the limit value is adjusted automatically by the program until the sum of the absolute differences between observed and calculated term values reaches a minimum. The results for the s-, p- and d-series of S VI show that the limit obtained in this way differs

less than 1 cm^{-1} from the value (710194.7 cm^{-1}) which was obtained from the f-, g- and h-series by means of a polarization formula. This value is also in good agreement with that obtained by Robinson from an isoelectronic analysis.

Transitions between hydrogen-like levels are much weaker in the present work than in beam-foil experiments. This fact depends largely on Stark effect line broadening in the spark source while the yrast levels are known to be considerably overpopulated in beam-foil spectroscopy. Thus, in our spectra the s-, p-, d- and f-series are observed up to higher n-values than the other series. The accuracy of the energies for these high levels gradually becomes poor since they are based on short-wave transitions. However, the existence of these transitions on the plates indicates that the spectrum has been excited very completely. This is also indicated by the fact that the electric quadrupole transition $3s^2S - 3d^2D$ corresponds to a line with good intensity which has also been found in Si IV and P V [6,8].

An isoelectronic comparison for the Na I-sequence is shown in Fig. 1. The diagram contains data up to Fe XVI with quantum numbers $n = 3 - 7$ and $\ell = 0 - 3$, [12]. The knowledge now reached is quite good except for Cl VII. As noted earlier the observations for S VI fit nicely into the diagram. The curves tend to run parallel as Z increases for a given n. This general feature of isoelectronic curves is an important tool in spectral analysis. The scaling factor $(Z - 10)$ was chosen so that curves with $n = 3$ will

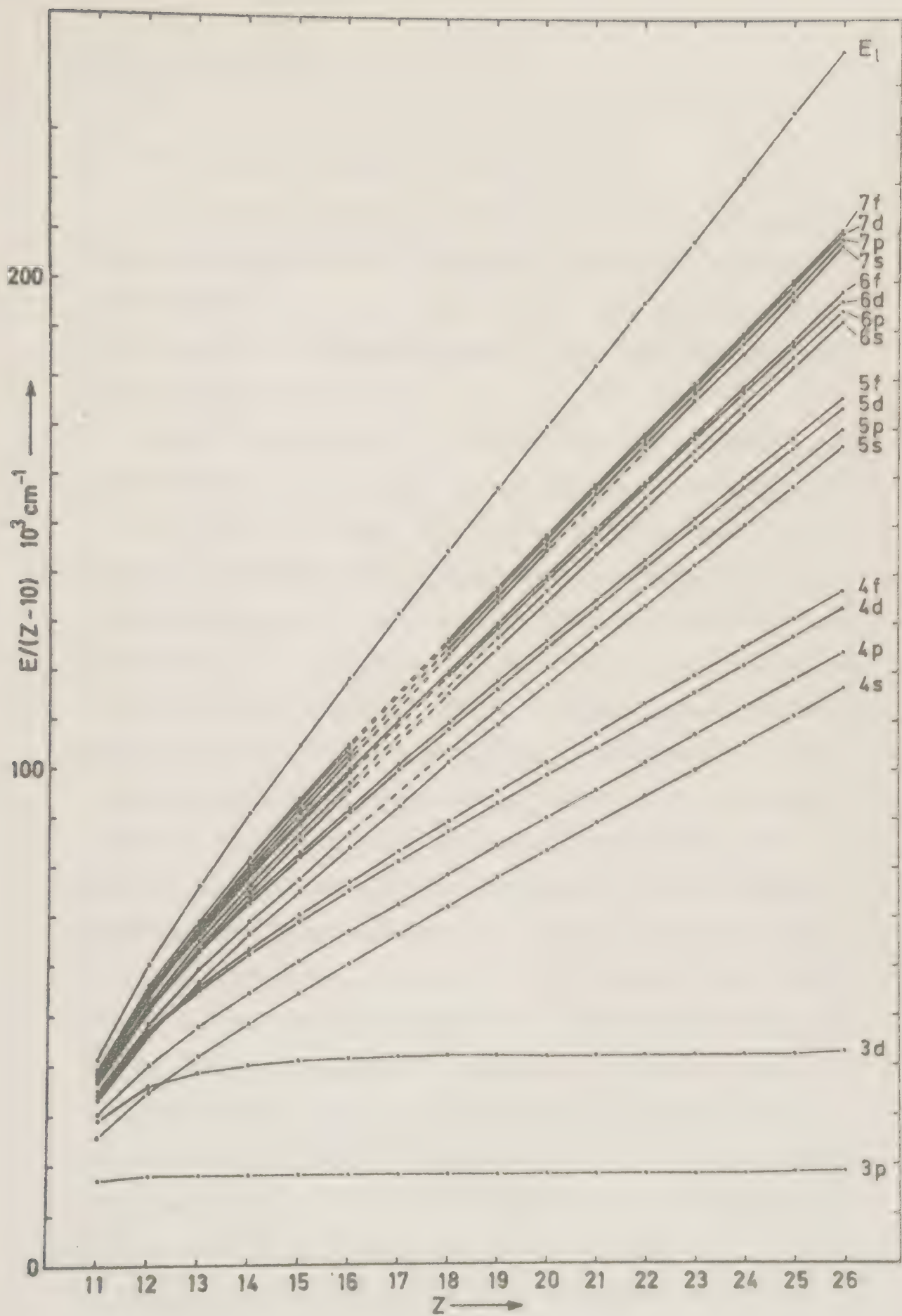


Fig 1. Isoelectronic comparison for the sequence Na I to Fe XVI

run horizontally.

4. The spectrum and term system of S V

S V belongs to the Mg I-sequence with two electrons outside closed shells. This gives a structure much more complicated than in the case of S VI. The result of our investigation is given in paper 2 (accepted for publication in *Physica Scripta*).

Most of the series in S V are affected by members of series belonging to higher limits. The singlet system of S V was quite difficult to analyse, which seems to be a general observation for singlet systems in two valence electron spectra. I used the same method as Magnusson and Zetterberg in P IV, analysing the singlet and triplet system in parallel. Analysis of the triplet system is simplified by the fine structure. Once a triplet term is found it may be used for estimating the position of the corresponding singlet. A great number of intersystem lines connect the singlet and triplet systems. Due to the many perturbations Ritz formulae are not as helpful for deriving the ionization limit as in S VI. However, the limit of S V can be deduced by means of a polarization formula for unperturbed members of the $3snh$ - and $3sni$ -series. In these hydrogen-like configurations the singlet-triplet splitting is too small to be resolved in our light-source. The adopted value for the ionization limit, 585514.1 cm^{-1} differs by 814 cm^{-1} from that given in [10].

Isoelectronic comparison provides a good tool when working with this kind of analysis. For the ions considered

here the Z-values are high enough for a smooth run of the curves. However, perturbations may cause irregularities in special cases. Perturbations can be nicely exposed by Ritz diagrams, especially if the positions of the perturbers are indicated in the diagrams. Parametric calculations (as discussed in paper 2) can also be used for finding terms and confirming identifications.

For the series belonging to the lowest limit the analysis now achieved should be complete enough for all practical purposes. Irregularities in the positions of some terms give hints where to look for some of the terms belonging to higher limits. Of the terms converging to the $3p^2 P$ limit the following were found: $3p^2 1S, 1D, 3P$; $3p4p 1S, 3S, 1P, 3P, 1D, 3D$; $3p3d$ and $3p4d 1P, 3P, 1D, 3D, 1F, 3F$; $3p4s 1P, 3P$. Furthermore, $3d^2 1D, 3P$ and $3F$ are observed as well as $3d^2 1G$ which is observed for the first time in the Mg I sequence.

The electric quadrupole transitions $3s^2 1S_0 - 3s3d 1D_2$, $3s^2 1S_0 - 3p^2 1D_2$ and $3s^2 1S_0 - 3s4d 1D_2$ are observed in S V as they were in P IV [17].

Sulphur has a relatively large cosmic abundance. Lines of S VI and S V are observed in the circumstellar envelope of some hot stars (e.g. ζ Puppis) [14,15,16] and the sun. Lines of sulphur spectra have also been observed in connection with volcanic activities on Jupiter's moon Io.

I would like to express my gratitude to Professors Bengt Edlén and Indrek Martinson who have supported and inspired me with their great knowledge and interest. I would

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